D E C L A R A T I O N

I, Ryuichi YAMADA, a Japanese Patent Attorney registered No. 7898 having my Business Office at Hasegawa Bldg., 4F, 7-7 Toranomon 3-chome, Minato-ku, Tokyo, Japan, solemnly and sincerely declare:

That I have a thorough knowledge of Japanese and English languages; and

That the attached pages contain a correct translation into English of the specification of the following Japanese Application:
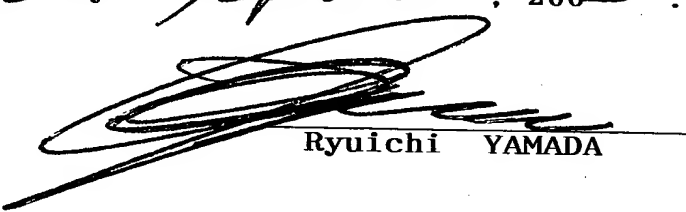
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Applicant(s)

CANON KABUSHIKI KAISHA

Signed this 25th day of September, 2003.

Ryuichi   YAMADA

PATENT OFFICE

JAPANESE GOVERNMENT

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Applicant(s)

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<TITLE OF THE INVENTION>
   ELECTROCONDUCTIVE ORGANIC COMPOUND DEVICE,
   ELECTROCONDUCTIVE LIQUID CRYSTAL DEVICE,
   AND ORGANIC ELECTROLUMINESCENCE DEVICE

<NUMBER OF CLAIMS> 10

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[Document]

Specification

[Title of the Invention]

Electroconductive Organic Compound Device,

ELECTROCONDUCTIVE LIQUID CRYSTAL DEVICE,

AND ORGANIC ELECTROLUMINESCENCE DEVICE

[CLAIMS]

1.   An electroconductive organic compound device, comprising:

a pair of oppositely spaced electrodes;

a carrier transporting layer, said carrier transporting layer disposed between said electrodes and in contact with one of said electrode;

wherein said carrier transporting layer comprises an electroconductive organic compound having a π-electron resonance structure in its molecule, and said π-electron resonance structure plane of said electroconductive organic compound in said carrier transporting layer is aligned in substantially parallel to an associated electrode surface.

2.   An electroconductive liquid crystal device, comprising:

a pair of oppositely spaced electrodes;

a carrier transporting layer, said carrier

transporting layer disposed between said electrodes and in contact with one of said electrode;

wherein said carrier transporting layer comprises an electroconductive liquid crystal having a π-electron resonance structure in its molecule, and said π-electron resonance structure plane of said electroconductive liquid crystal in said carrier transporting layer is aligned in substantially parallel to an associated electrode surface.

3. An organic electroluminescence device, comprising: an electroconductive liquid crystal as defined in Claim 2; and a luminescent organic layer disposed in a pair of oppositely spaced electrodes.

4. An organic electroluminescence device according to Claim 3, wherein said luminescent organic layer and said carrier transporting layer comprising said electroconductive liquid crystal have been formed by vacuum deposition on an electrode.

5. An organic electroluminescence device according to Claim 3 or 4, wherein said π-electron resonance structure plane of said electroconductive organic compound device (or said electroconductive liquid crystal) in said carrier transporting layer is aligned in substantially parallel to an associated

electrode surface by a heating treatment of said device.

6. An organic electroluminescence device according to Claim 4, wherein said luminescent organic layer is assumed to have an amorphous state.

7. An organic electroluminescence device according to any one of Claims 3 to 6, wherein said electroconductive liquid crystal includes a discotic liquid crystal.

8. An organic electroluminescence device according to Claim 7, wherein said electroconductive liquid crystal is a liquid crystal having a discotic disordered phase or a liquid crystal phase having a lower order than said discotic disordered phase.

9. An organic electroluminescence device according to any one of Claims 3 to 6, wherein said electroconductive liquid crystal includes a smectic liquid crystal.

10. An organic electroluminescence device according to Claim 9, wherein said electroconductive liquid crystal is a liquid crystal having a SmE phase or a liquid crystal phase having a lower order than

SmE phase.

[Detailed Description of the Invention]
[Field]

The present inventions to an
(electro)conductive organic compound device used in
electronic devices, an (electro)conductive liquid
crystal device, and an organic electroluminescence
device using the liquid crystal device.
[Prior Art]

As for organic electroluminescence devices
(hereinafter, the term "electroluminescence" being
sometimes abbreviated as "EL" according to a common
usage in the field), carrier injection-type EL devices
utilizing organic solids, such as anthracene single
crystal, were studied in detail. These devices were
of a single layer-type, but thereafter Tang, et al
proposed a lamination-type organic EL device
comprising a luminescent layer and a hole transporting
layer between a hole injecting electrode and an
electron injecting electrode. The luminescence
mechanism in these injection-type EL devices commonly
includes stages of (1) electron injection from a
cathode and hole injection from an anode, (2) movement
of electrons and hales within a solid, (3) re-
combination of electrons and holes, and (4) luminance
from single term excitons.

A representative example of the lamination-type EL device may have a structure including an ITO film as a cathode formed on a glass substrate, a ca. 50 nm-thick layer formed thereon of TPD (N,N'-diphenyl-N,N'-di(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine) having a structure of a formula shown below, a ca. 50 nm-thick layer thereon of Alq3 (tris(8-quinolinolato)-aluminum), and further a vapor deposition layer of Al-Li alloy as a cathode.

TPD
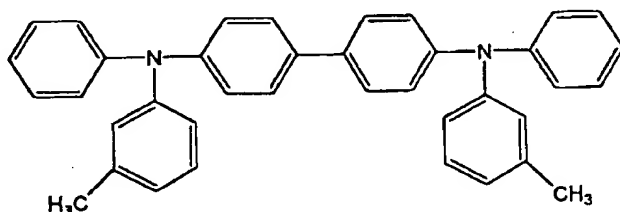
By setting the work function of the ITO used as the anode at 4.4 - 5.0 eV, the hole injection to TPD is made easier, and the cathode is composed of a metal which has as small a work function as possible and also is stable. Examples of the cathode metal may include Al-Li alloy as mentioned above and also Mg-Ag alloy. By the above organization, green luminescence may be obtained by applying a DC voltage of 5 - 10 volts.

An example using an electroconductive liquid crystal as a carrier transporting layer is also known. For example, D. Adam et al (Nature, Vol. 371, p. 141-) have reported that a long-chain triphenylene compound

as a discotic liquid crystal material exhibited a mobility of 10^{-3} - 10^{-2} cm^2/V.sec in its liquid crystal phase (Dh phase) and a mobility of 10^{-1} cm^2/V.sec in its mesophase (an intermediate phase, not a liquid crystal phase). Also, as for a bar-shaped liquid crystal, Junichi Hanna (Ohyou Butsuri (Applied Physics), Vol. 68, No. 1, p. 26-) has reported that a phenylnaphthalene compound exhibited a mobility of 10^{-3} cm^2/V.sec or higher in its smectic B phase.

As a trial for using such a liquid crystal for electroluminescence, INGAH STAPFF et al. (Liquid Crystals, Vol. 23, No. 4, pp. 613-617) have reported an organic EL device using a triphenylene-type discotic liquid crystal. Other reports are found in POLYMERS FOR ADVANCES TECHNOLOGIES, Vol. 9, pp. 463-460 (1998), and ADVANCED MATERIALS (1997), Vol. 9, No. 1, p. 48.

[Problems to be Solved]

An organic layer in a conventional organic EL device has been of a monomeric amorphous type and has been formed by vacuum evaporation process, so that it has been difficult to provide a thickness in excess of 1 μm in view of the productivity. Accordingly, the total thickness of the organic layers has generally been as thin as 100 nm - 200 nm, and this has been accompanied with several problems.

More specifically, as the organic layers are

thin, an electrical short circuit is liable to occur between the electrodes. Further, due to the necessity of carrier injection, an insulating layer cannot be inserted unlike in inorganic EL devices for obviating the above problem. As a result, the organic EL device has involved a problem regarding drive stability as an electronic device.

Further, as the organic layers between the electrodes are thin, the device capacitance is increased to cause a large drive current. This incurs an increase in power consumption and is not desirable.

Moreover, as briefly mentioned above, in a conventional organic EL device, a high electric field (on the order of 10 V/100 nm) has been required for drive because of low performances of injection of electrons and holes from the electrodes, such as ITO, to the organic layers. As organic materials used in an organic EL device has a band gap as broad as ca. 3.0 eV or more, thermal excitation-type free electrons are not present in a conduction band (or LUMO: Lowest Unoccupied Molecular Orbital), a drive current is principally supplied by a tunnel current injected from the electrodes. The injection efficiency of the current is known to be remarkably affected not only by the work functions of the electrodes and a level gap between LUMO and HOMO (Highest Occupied Molecular Orbital) of the organic materials but also by the

molecular alignment and structure of the organic materials. For example, in the case where organic molecules assume a crystalline state, minute crystalline boundaries function as carrier conduction obstacles, so that organic materials are generally used in an amorphous state, but only a low carrier injection efficiency is available in this case.

For the above reason, in order to attain a sufficient drive current by using ordinary organic compounds (such as TPD, α-NPD (bis[N-(1-naphthyl)-N-phenyl]benzidine), TAZ-01(3-(4-biphenylil)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazol), Alq3, etc.) in ordinary EL devices, it has been necessary to apply a high electric field (on the order of 10 V/100 nm) across the organic layer-electrode boundaries. Further, as the mobility of the organic materials is on the order of 10^{-3} - 10^{-5} $cm^2/V.cm$, it is also necessary to apply a high electric field in order to ensure a drive current.

The application of such a high electric field leads to the necessity of thin device layers, which also leads to an electrical short circuit between the electrodes and an increase in capacitance load.

Further, an organic EL device is liable to be affected by invaded moisture to cause deterioration of luminance performance and drive performance, thus showing poor durability. In an ordinary organic EL

device, the organic layers are disposed in lamination and then the cathode is formed thereon by vapor deposition process of a metal film. In this instance, a metal species having a small work function suitable for the cathode is susceptible of oxidation and has a low durability. Even in case of forming a protective film thereon by sputtering, the organic layers are liable to be degraded if the forming temperature is high (with an ordinary limit of 100 ^{O}C), and the destruction of the device structure due to the film stress is also problematic.

Accordingly, it is a principal object of the present invention to provide improvements to problems as mentioned above encountered in organic EL devices proposed heretofore, and to provide an organic EL device which requires a small power consumption and is excellent in reliability and durability. More specifically, it is another object of the present invention to realize a carrier transporting layer exhibiting a high carrier injection efficiency from an electrode to the organic layers, thus providing an organic EL device rich in durability by using thick organic layers including the carrier transporting layer.

[Means for Solving the Problems]

In accordance with a principal aspect of the present invention, there is provided an

electroconductive organic compound device, comprising: a pair of oppositely spaced electrodes; a carrier transporting layer, the carrier transporting layer disposed between the electrodes and in contact with one of the electrode; and wherein the carrier transporting layer comprises an electroconductive organic compound having a π-electron resonance structure in its molecule, and the π-electron resonance structure plane of the electroconductive organic compound in the carrier transporting layer is aligned in substantially parallel to an associated electrode surface.

In accordance with another aspect of the resent invention, there is provided an electroconductive liquid crystal device, comprising: a pair of oppositely spaced electrodes; a carrier transporting layer, the carrier transporting layer disposed between the electrodes and in contact with one of the electrode; and wherein the carrier transporting layer comprises an electroconductive liquid crystal having a π-electron resonance structure in its molecule, and the π-electron resonance structure plane of the electroconductive liquid crystal in the carrier transporting layer is aligned in substantially parallel to an associated electrode surface. More particularly, the electroconductive liquid crystal device of the present invention used

the liquid crystal as an electroconductive organic compound in the above-mentioned electroconductive organic compound device of the present invention.

In accordance with a further aspect of the present invention, there is an organic electro-luminescence device, comprising: the above-mentioned electroconductive liquid crystal of the present invention; and a luminescent organic layer disposed in a pair of oppositely spaced electrodes.

In the above-mentioned organic electroluminescence device, it is desirable that the luminescent organic layer and the carrier transporting layer comprising the electroconductive liquid crystal have been formed by vacuum deposition on an electrode, and it is also desirable that the π-electron resonance structure plane of the electroconductive liquid crystal (or the luminescent organic layer) in the carrier transporting layer is aligned in substantially parallel to an associated electrode surface by a heating treatment, and it is desirable that the luminescent organic layer is assumed to have an amorphous state.

Further in the above-mentioned organic electroluminescence device, it is desirable that the electroconductive liquid crystal includes a discotic liquid crystal, and it is desirable that the electroconductive liquid crystal is a liquid crystal

having a discotic disordered phase or a liquid crystal phase having a lower order than the discotic disordered phase or, it is desirable that the electroconductive liquid crystal includes a smectic liquid crystal, and it is also desirable that the electroconductive liquid crystal is a liquid crystal having a SmE phase or a liquid crystal phase having a lower order than SmE phase.

According to a first embodiment of the present invention, an (electro)conductive organic compound having a π-electron resonance structure in its molecule is used to form a carrier transporting layer wherein the π-electron resonance structure plane of the electroconductive organic compound is aligned in substantially parallel to an associated electrode surface, thereby improving the carrier injection performance from the electrode boundary. An electro conductive organic compound device, particularly an electro conductive liquid crystal device using an electro conductive liquid crystal as the electroconductive organic compound, including such a carrier transporting layer, can be applied to electronic devices, such as a photo-sensor, a photoconductor (for constituting, e.g., a photosensitive drum for copying machines), an organic semiconductor device (such as an organic TFT (thin film transistor)), a temperature sensor, and a spatial

modulation device, and particularly preferably to an organic EL device.

If an electroconductive liquid crystal is used as the electroconductive organic compound for constituting a carrier transporting layer, it becomes easy to align the π-electron resonance structure plane thereof parallel to the associated electrode surface. The electroconductive liquid crystal aligned in this manner can take advantage of the following effects.

(1) Some electroconductive liquid crystals have a mobility exceeding 10^{-2} cm^2/V.sec (D. Adam, et al; Nature, Vol. 371, p. 141-).

(2) An electro conductive liquid crystal has an alignment characteristic by causing a phase transition into smectic phase, nematic phase or isotropic phase at high temperatures and can be used in an aligned state as in an ordinary liquid crystal device used for display. By utilizing such an alignment characteristic, a thick organic layer can be formed. Further, by adopting a cell structure using oppositely disposed glass substrates, it is possible to prevent the deterioration due to invasion of moisture, etc.

(3) In the case of using a discotic liquid crystal as an electroconductive liquid crystal, a discotic liquid crystal generally has a structure including a core of, e.g., triphenylene, and side chains attached to the periphery of the core for

developing mesomorphism (liquid crystal property).
The side chains generally exhibit poor wettability
with a substrate of a metal or a metal oxide (such as
ITO), so that in the liquid crystal state of the
discotic liquid crystal, the core is aligned parallel
to the electrode surface, whereby the π-electron
resonance structure plane of the core is aligned
parallel to the electrode surface, thereby
facilitating carrier transfer with the electrode.
Accordingly, it is possible to provide a higher
injection efficiency than an ordinary organic compound
in an amorphous state.

In this way, by aligning a discotic liquid
crystal having hydrophobic side chains relative to an
electrode surface, it is possible to improve the
efficiency of carrier injection from the electrode to
the organic layers. This effect can also expected for
an ordinary bar-shaped liquid crystal having a
molecular structure including a phenyl group or a
naphthalene group having a π-electron resonance
structure plane, and the alignment of such a π-
electron resonance structure can improve the
interaction with electron cloud given by atoms of the
electrode, thereby improving the carrier injection
from the electrode.

(4) A molecule exhibiting mesomorphism can change
a molecular disposition relative to an electrode

surface by a realigning post-treatment. This can also facilitate the injection efficiency.

[Description of the Preferred Embodiments]

Hereinafter, the structure of the present invention will be described more specifically and concretely.

In the present invention, the π-electron resonance structure of the electroconductive organic compound or the electroconductive liquid crystal constituting the carrier transporting layer is generally given by an aromatic ring, examples thereof may include: triphenylene ring, naphthalene ring and benzene ring, as representative, and also pyridine ring, pyrimidine ring, pyridazine ring, pyrazine ring, tropone ring, azulene ring, benzofuran ring, indole ring, indazole ring, benzothiazole ring, benzoxazole ring, benzimidazole ring, quinoline ring, isoquinoline ring, quinazoline ring, quinoxaline ring, phenanthrene ring and anthracene ring.

The electroconductive liquid crystal used in the present invention may preferably comprise a discotic liquid crystal or a smectic liquid crystal. A discotic liquid crystal may generally have a core structure which may be given by an aromatic ring as mentioned above for the π-electron resonance structure, as represented by triphenylene ring (or skeleton). Further examples thereof may include

truxene skeleton, metal-phthalocyanine skeleton, phthalocyanine skeleton, dibenzopyrene skeleton, metal-phthalocyanine skeleton, dibenzopyrene skeleton, and hexabenzocoronene skeleton.

The discotic liquid crystal used in the present invention may preferably be a liquid crystal having a discotic disordered phase or a liquid crystal phase having a lower order than the discotic disordered phase. More specifically, it is preferred to use a liquid crystal having a discotic disordered phase or a discotic nematic phase.

Examples of the discotic liquid crystal may include the liquid crystal Compounds of triphenylene system 1 - 5 represented by the following structural formulae (as shown in Advanced Materials, 1996, 8, No. 10).

HHOT
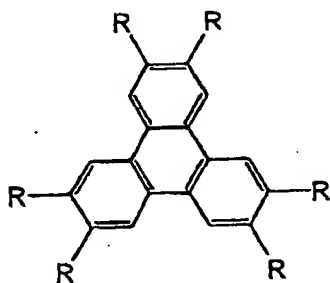
R: $C_8H_{12}O$

To supplement, the discotic liquid crystal phases may be classified into discotic nematic phase

and discotic columnar phase, and the discotic columnar phase is further divided into discotic disordered phase and discotic ordered phase which has a higher order than the discotic disordered phase.

A higher mobility is exhibited by a liquid crystal having discotic ordered phase, but in view of a carrier injection performance from an electrode surface, a liquid crystal having discotic disordered phase can exhibit a better performance because of its better alignability of π-electron resonance structure plane parallel to the electrode surface according to the present invention, thus being preferably used to constitute a carrier transporting layer according to the present invention.

Incidentally, in the case of passing across a layer of organic compound sandwiched between a pair of electrodes, the carrier injection is effected by a tunnel current or a Schottky current depending on an energy barrier at the injection boundary. And, if the injection barrier is sufficiently low and the carrier is sufficiently injected, the current is flowed as a spatial charge controlling current proportional to the mobility. Accordingly, in order to perform an effective current flow, it is preferred to improve the injection performance at a proximity to the boundary and use a material having an internally large mobility.

Accordingly, in the case of using a discotic liquid crystal for a carrier transporting layer, it is also preferred to use a two layer-structured liquid crystal layer including a lamination of a layer of discotic liquid crystal showing discotic disordered phase at the boundary with the electrode and a layer of discotic liquid crystal showing discotic ordered phase on a remoter side from the electrode. As such a discotic liquid crystal having discotic ordered phase, HBOT (hexabisbutyloxytriphenylene) represented by the following formula may for example be preferably used.

HBOT
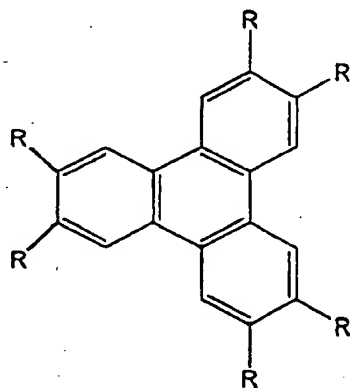
R: C_4H_9O

On the other hand, the smectic liquid crystal used in the present invention may preferably be a smectic liquid crystal having SmE phase or a smectic phase of a lower order than SmE phase. More specifically, it is preferred to use a liquid crystal having SmE phase or SmB phase. As such a smectic

liquid crystal having SmE phase, PN84 (2-butoxy-6-(3-octylphenyl)naphthalene) may for example be preferably used.

PN84

$$C_8H_{17} - \bigcirc - \bigcirc - \bigcirc - OC_4H_9$$
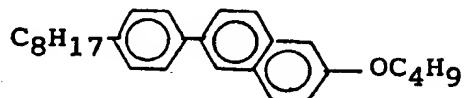
The carrier transporting layer of an electroconducive liquid crystal according to the present invention may be formed by vacuum deposition process on an electrode. The layer of electroconductive liquid crystal after the vacuum deposition is assumed to have an amorphous state, i.e., isotropic, indefinite and bulky alignment state. Liquid crystal molecules in such an alignment state can readily cause an alignment change at a liquid crystal phase temperature. Accordingly, in a device including a carrier transporting layer formed by vacuum deposition of an electroconductive liquid crystal, it is possible to easily re-align the π-electron resonance structure phase parallel to an associated electrode surface by an appropriate heating treatment, thereby attaining a high carrier injection efficiency.

As for the electrode materials used in the present invention, examples of the anode materials may include: indium oxide, tin oxide, Cd_2SnO_4, zinc oxide,

copper iodide, gold and platinum, in addition to ITO. Examples of the cathode materials may include: alkali metals, alkaline earth metals and alloys of these, inclusive of sodium, potassium, magnesium, lithium, sodium-potassium alloy, magnesium-indium alloy, magnesium-silver alloy, aluminum, aluminum-lithium alloy, aluminum-copper alloy, aluminum-copper-silicon alloy.

Further, examples of materials for the luminescent organic layer may include: in addition to Alq3, BeBq (bis(benzoquinolinolato)beryllium), DTVB2 (4,4'-bis(2,2-di-p-tolylvinyl)biphenyl), Eu(DBM)3(Phen)(tris(1,3-diphenyl-1,3-propanediono)-monophenanthroline)Eu(III)), and further, diphenyl-ethylene derivatives, triphenylamine derivatives, diaminocarbazole derivatives, bisstyryl derivatives, benzothiazole derivatives, benzoxazole derivatives, aromatic diamine derivatives, quinacridone compounds, perylene compounds, oxadiazole derivatives, coumarin compounds, and anthraquinone derivatives. These materials are preferably formed in an amorphous state by vacuum deposition process.

Figure 1 is a schematic sectional view showing a basic structure of an embodiment of the organic EL device according to the present invention. Referring to Figure 1, the organic EL device includes an anode 1, a carrier transporting layer 3, a

luminescent organic layer 4 and a cathode 2, laminated
in this order. In this embodiment, the carrier
transporting layer 3 comprises a hole-transporting
conductive liquid crystal having HOMO close to the
energy level of ITO constituting the anode 1 and is
disposed in contact with the anode 1. A carrier
transporting layer comprising an electroconductive
liquid crystal having an electron-transporting
characteristic and disposed in contact with the
cathode 2 is expected to have a similar effect of
improving the carrier injection from the electrode.

(Example 1)

An organic EL device having a sectional
structure as shown in Figure 2 was prepared. Figure 2
shows a similar structure as in Figure 1 but shows a
glass substrate 5 supporting the anode 1 and luminance
layers 4a, 4b and 4c of different colors instead of
the single luminance layer 4 in Figure 1.

More specifically, on a glass substrate 1
held at 200 $^{\circ}$C, a 70 nm-thick ITO film was formed as a
hole-injecting anode 1 by sputtering using a target of
In 90 % and Sn 10 % while flowing Ar gas at 200 sccm
and O$_2$ gas at 3 sccm. The ITO film showing a work
function of ca. 4.35 eV was exposed to ultraviolet
rays from a low-pressure mercury lamp to have an
elevated work function of 4.60 eV.

The above-treated substrate having an ITO

film was placed in a vacuum chamber held at a pressure below 2×10^{-5} torr, and a ca. 50 nm-thick layer of HHOT (hexabishexyloxytriphenylene) was formed on the ITO film as a carrier transporting layer 3 by vacuum deposition process at a rate of ca. 0.1 nm/sec at a pressure of 1×10^{-5} torr according to the resistance heating vacuum deposition method. HHOT exhibited a mobility of 1×10^{-3} $cm^2/V \cdot sec$ at ca. 70 ^{O}C or below according to the time-of-flight method when sandwiched in a 15 μm-thick layer between a pair of ITO substrates. Incidentally, HHOT is a discotic liquid crystal causing a transition from crystal to discotic disordered phase at 65 ^{O}C and a transition to isotropic phase at 98 ^{O}C.

Luminescent organic layer segments 4a - 4c exhibiting different luminescent wavelengths were respectively formed in a thickness of 50 nm on the HHOT layer 3 by vacuum deposition process through a mask under the conditions of a pressure of 1×10^{-5} torr and a deposition rate of ca. 0.1 mm/sec. The organic layers 4a - 4c were respectively formed of Alq3 alone, Alq3 doped with 5 wt. % of perylene for shifting the luminescence wavelength to a shorter wavelength side, and Alq3 doped with 5 wt. % of DCM (a styryl dye) for shifting to a longer wavelength side. The structural formulae for the above-mentioned Alq3 perylene and DCM are shown below.
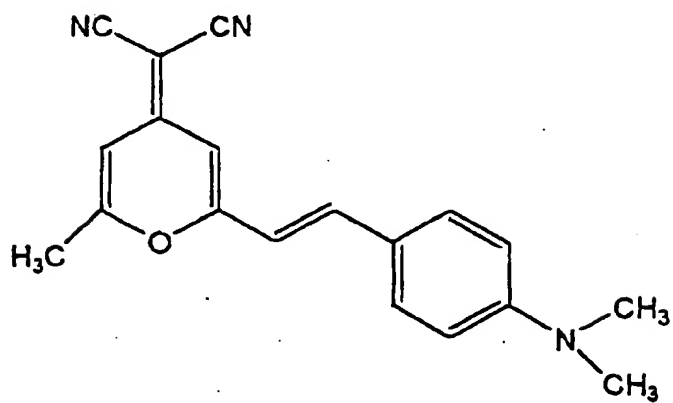
Alq3
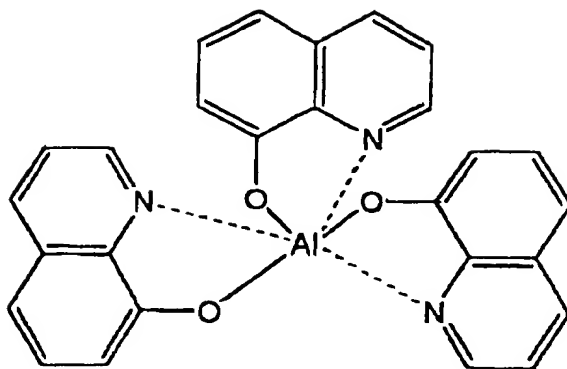
perylene
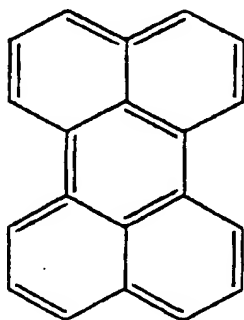
DCM

The above-prepared luminescent organic layers 4a - 4c were respectively coated with cathode metals 2 each comprising a 50 nm-thick layer of Al-Li alloy (Li content = 1.8 wt. %) film and a 150 nm-thick Al layer, respectively formed by vacuum deposition, to obtain an organic EL device having a structure of the first embodiment of the present invention. The device was heated to 65 ^{O}C, whereby electroluminescent was realized at an increased current at that temperature. In the device at 65 ^{O}C, it was confirmed that the liquid crystal in the carrier transporting layer 3 on the ITO electrode 2 was aligned so that the discotic columns thereof were aligned in substantially vertical to the electrode surfaces (re-alignment effect: The liquid crystal alignment was confirmed by using a sample device having a layer structure of a 10 nm cathode metal formed by vacuum deposition and observing the sample device through a right-angle cross nicol polarizing microscope. A similar alignment was confirmed also when the HHOT layer thickness was increase to 150 nm).

(Example 2)

On a glass substrate, a 70 nm-thick ITO film was formed by sputtering similarly as in Example 1 and then subjected to an oxygen-plasma treatment under the conditions of O_2 gas flow rate of 200 sccm, a pressure of 10 m.torr, a power of 400 W and a treatment time of

4 min., whereby the ITO film was caused to have an elevated work function of ca. 4.93 eV.

The above-treated substrate having an ITO film was coated with a carrier transporting layer comprising a lamination of a 20 nm-thick HHOT layer and a 50 nm-thick HBOT layer. The HHOT layer and the HBOT layer were respectively formed by the resistance heating vacuum deposition method at a pressure of 1×10^{-5} torr and a deposition rate of ca. 0.1 mm/sec successively in the same vacuum chamber with an intermediate re-evacuation step. HBOT exhibited a mobility of 1×10^{-2} cm^2/V.sec at ca. 70 $^\circ$C or below according to the time-of-flight method. HBOT is a discotic liquid causing a transition from crystal to discotic ordered phase at 89.4 $^\circ$C and a transition to isotropic phase at 144.7 $^\circ$C.

Then, luminescent organic layers 4a - 4c and cathode metals 5 were formed in the carrier transporting layer 3 similarly as in Example 1 to obtain an organic EL device. The device was heated to 75 $^\circ$C, whereby electroluminescence was realized at an increased current at that temperature.

(Comparative Example 1)

An organic EL device was prepared in the same manner as in Example 2 except that a carrier transporting layer was formed on the ITO layer by first forming a 20 nm-thick HBOT layer and then

forming a 50 nm-thick HHOT layer thereon.

(Comparative Example 2)

A glass substrate was coated with an ITO film and treated by UV treatment in the same manner as in Example 1.

The ITO film on the substrate was further coated with a carrier transporting layer comprising in lamination a 20 nm-thick layer of CuPc (copper-phthalocyanine) having a structure represented by a formula below and a 50 nm-thick layer of HHOT respectively formed by vacuum deposition under conditions similar to those adopted for the vacuum deposition of the HHOT layer in Example 1.

CuPc
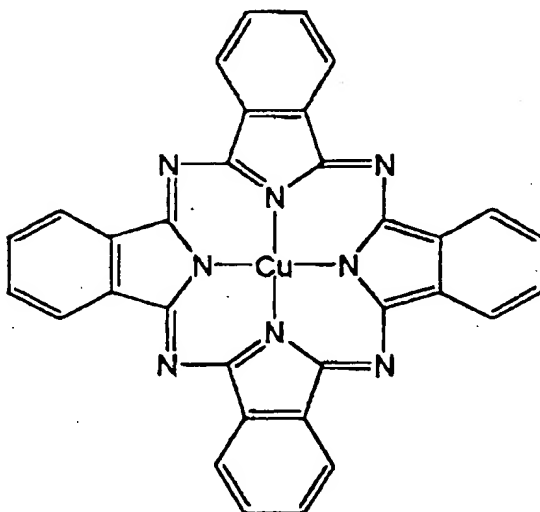
Then, luminescent organic layers 4a - 4c and cathode metals 2 were formed on the carrier

transporting layer 3 similarly as in Example 1 to obtain an organic EL device.

The above-prepared 4 devices of Examples 1 – 2 and Comparative Examples 1 – 2 were respectively supplied with an electric field of 12 V/100 nm at various temperatures to measure a current density. The results are inclusively shown in Table 1 below.

Table 1

Example	Layer structure	Temp. (^{o}C)	Current density ($\mu A/cm^2$) 12V/100nm	Current ratio
1	ITO/HHOT/Alq3 /AlLi/Al	30	50	1
		65	3593	71.9
2	ITO/HHOT/HBOT /Alq3/AlLi/Al	30	50	1
		65	3500	70.0
Comp.1	ITO/HHOT/HHOT /Alq3/AlLi/Al	30	140	2.8
		90	600	12.0
Comp.2	ITO/CuPc/HHOT /Alq3/AlLi/Al	30	1136	22.7
		65	1145	22.9

As is shown in Table 1 above, the device of Example 1 exhibited only a low current density of 50 $\mu A/cm^2$ at 30 ^{o}C (crystal phase temperature for HHOT) where HHOT was presumably in an amorphous state after

the vacuum deposition, but exhibited a remarkably increased current density of 3593 $\mu A/cm^2$ when heated to 65 ^oC (to 68 ^oC) where it was confirmed that HHOT was placed in discotic disordered phase and in a homeotropic alignment state where the director (defined as a vector perpendicular to a π-electron resonance structure plane of a core of a discotic liquid crystal) of HHOT was perpendicular to the ITO film between the ITO film and the Alq3 film. This means that the π-electron resonance structure plane of HHOT was aligned in parallel to the ITO electrode surface. Incidentally, a discotic liquid crystal has a negative refractive index anisotropy, so that no phase difference is formed in a direction perpendicular to the electrode surface when the discotic liquid crystal is placed in the homeotropic alignment state where the above-defined director is aligned normal to the electrode surface. For this reason, an alignment state of a discotic liquid crystal can be specified through a polarizing microscope observation.

On the other hand, the device of Comparative Example 1 exhibited a current density of 140 $\mu A/cm^2$ at 30 ^oC somewhat higher than the device of Example 1. This is presumably because HBOT having a mobility higher by one digit than HHOT was used in Comparative Example 1.

The device of Comparative Example 1 did not exhibit a remarkable increase in current density unlike the device of Example 1 when heated to 90 ^{O}C. This is presumably because HBOT assumes discotic ordered phase at 90 ^{O}C and does not have discotic disordered phase. As a result of observation of actual alignment state in a device, HHOT assumes a homeotropic alignment state wherein the director is aligned in agreement with a normal to the substrate as mentioned above, whereas HBOT does not readily assume a homeotropic alignment state but assumes a substantially random alignment state.

On the other hand, the device of Example 2 caused a remarkable increase in current density similarly as in Example 1 when heated to 65 ^{O}C. This may be attributable to an improvement in carrier injection efficiency at the boundary between the ITO film and the HHOT layer due to alignment of HHOT.

In the device of Example 2, the increase in current density was observed in some cases even at a temperature somewhat below the phase transition temperature (65 ^{O}C) where the liquid crystal portion was not considered to completely form a homeotropic alignment. This may be attributable to a feature that a microscopic alignment change favoring the improvement in carrier injection at the electrode boundary can be relatively easily caused in discotic

disordered phase.

On the other hand, the device of Comparative Example 2 including a 20 nm-thick CuPc layer inserted between the ITO electrode and the HHOT layer exhibited a remarkably larger current density of 1136 $\mu A/cm^2$. This is presumably because CuPc has a HOMO of 4.09 eV lower than an HHOT's HOMO of 5.13 eV and provided a reduced energy barrier of 0.09 eV reduced from 0.53 eV relative to the ITO's work function of 4.60 eV.

However, the device of Comparative Example 2 did not cause a substantial increase in current density even when heated to 65 - 68 ^{O}C. This is presumably because CuPc have no liquid crystal phase is a temperature range of 65 - 68 ^{O}C, and a carrier injection efficiency improvement by re-alignment of π-electron resonance structure plane as in the device of Example 1 cannot be expected. Incidentally, in a device having a layer structure of ITO/HHOT/CuPc/Alq3/AlLi including a layer order reverse from ITO/CuPc/HHOT ... in the device of Comparative Example 2, an increase in current density accompanying a temperature increase was observed similarly as in Example 1. Accordingly, the current density increase due to a temperature increase may be attributable to an improvement in carrier injection efficiency at the ITO/HHOT boundary.

(Example 3)

An organic EL device was prepared in the same manner as in Example 1 except that a 50 nm-thick layer of PN84 (a bar-shaped smectic liquid crystal) was formed by vacuum deposition process instead of the HHOT layer under the conditions of a pressure of 1×10^{-5} torr and a deposition rate of ca. 0.1 nm/sec.

PN84 causes a phase transition from crystal phase to SmE phase (liquid crystal phase) at 68.7 $^{\circ}$C, a phase transition from SmE phase to SmA phase (liquid crystal phase), and a phase transition of SmA phase to isotropic phase at 131.1 $^{\circ}$C, and also exhibits a mobility of ca. 10^{-3} cm^2/V.sec in SmE phase.

The device was heated to 69 $^{\circ}$C, whereby good electroluminescence was obtained. At this time, PN84 assumed a homogeneous alignment state wherein the director thereof was aligned parallel to the ITO electrode surface but in random directions between the ITO electrode and the Alq3 layer. In the case of a bar-shaped liquid crystal like PN84, a director is taken in a molecular long-axis direction so that the director alignment in the carrier transporting layer parallel to the electrode surface provides an organic EL device wherein the π-electron resonance structure plane of the liquid crystal is aligned parallel to the electrode surface.

[Advantageous Effect]

As described in the foregoing, according to

the present invention, by using the electroconductive organic compound device of the present invention or the electroconductive liquid crystal device having a carrier transporting layer exhibiting a high carrier injection efficiency, it is possible to constitute an electronic device requiring a reduced power consumption. According to the organic EL device of the present invention which applies the electroconductive liquid crystal device, the total thickness of the organic layers including the electroconductive liquid crystal layer can be increased, so that it is possible to provide a reliable organic EL device. Further, by forming a cell structure including a glass substrate or the like, it is possible to provide an organic EL device having a high durability.

[Brief Description of the Drawings]

Figure 1 is a schematic sectional view for illustrating a basic structure of an organic EL device according to an embodiment of the invention.

Figure 2 is a schematic sectional view of an organic EL device prepared in an Example of the invention.

[Reference Numerals]

1:    anode

2:    cathode

3:     carrier transporting layer

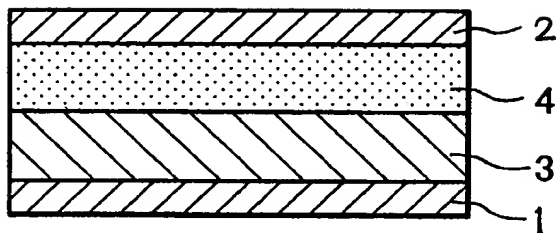4, 4a, 4b, 4c: luminescent organic layer

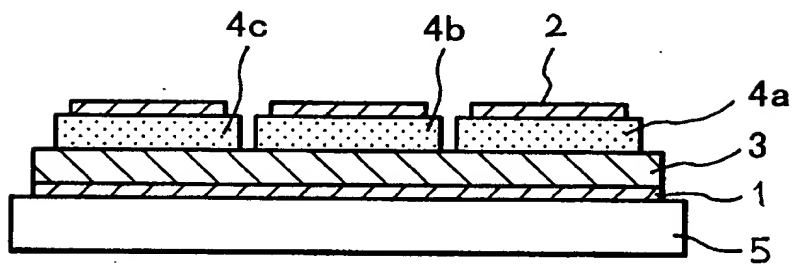5:   glass substrate

FIG. 1

FIG. 2

[Document]

Abstract

[Abstract]

[Object]

It is a principal object of the present invention to provide a novel organic electroluminescence device capable of preventing from being occurred an electrical short-circuit between an anode and a cathode and capable of improvement of a carrier injection efficiency from an electrode to a luminescent organic layer.

[Means for Solving]

There is provided an organic electroluminescence device wherein a carrier transporting layer comprising a discotic liquid crystal having a discotic disordered phase or a liquid crystal phase having a lower order than the discotic disordered phase, or a smectic liquid crystal having a SmE phase or a liquid crystal phase having a lower order than SmE phase is formed, and is placed in contact with one of the electrodes, and wherein the carrier transporting layer was heated to the temperature enough to assume the liquid crystal phase in the liquid crystal, whereby a π-electron resonance structure plane of the electroconductive organic compound (or the electroconductive liquid crystal) in the carrier transporting layer is aligned in

substantially parallel to an associated electrode
surface.

[Selected Figure]

Nothing